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A NEW CLASS OF DISULPHONES

A DISSERTATION
PRESENTED TO THE FACULTY OF BRYN MAWR COLLEGE
FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

BY

MARGARET BAXTER MACDONALD

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A NEW CLASS OF DISULPHONES

By a comparison of the compounds of carbon and sulphur many striking analogies are brought to light. These are seen most clearly when carbon compounds are compared with those organic sulphur compounds which contain quadrivalent or hexavalent sulphur, as for example, sulphonic acids and sulphones.

The sulphonic acids form chlorides, substitution products, anhydrides and salts which resemble closely the corresponding derivatives of carbonic acids in composition, structure and essential properties. The analogy between ketones and sulphones is more striking even than that of sulphonic and carbonic acids. The simple sulphones, RSO_2R, like the corresponding ketones, RCOR, are indifferent substances, which boil without decomposition, and which are not readily attacked by reagents. Polyketones are much more reactive than monoketones. All 1, 3 diketones and 1, 3 ketonic acid esters for example, are readily hydrolyzed according to the equations:

$$RCO.CH_2.COR + H_2O = RCOCH_3 + RCOOH.$$
$$RCO.CH_2.COOR + H_2O = RCOCH_3 + ROH + CO_2$$

All 1, 3 sulphone ketones and 1, 3 sulphone carbonic acid esters behave in exactly the same way:

$$RSO_2CH_2COR + H_2O = RSO_2CH_3 + RCOOH$$
$$RSO_2CH_2COOR + H_2O = RSO_2CH_3 + ROH + CO_2\,.$$

In these reactions the RSO_2-group is exactly equivalent to the RCO-group.

The 1, 3 disulphones are more stable than the corresponding diketones and sulphone ketones; but like the latter they form metallic derivatives in which the metal is replaceable by hydrocarbon residues.

The researches of Otto,[1] Baumann,[2] Autenried,[3] and Posner[4] have led to the discovery of the sulphur analogues of nearly all classes of polyketones. The only important class that is missing is that of 1,2 disulphones;

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[1] Ber. d. chem. Ges., **18**, 154; **21**, 89; **18**, 2493.

[2] Ber. d. chem. Ges., **19**, 2806.

[3] Ber. d. chem. Ges., **24**, 1891.

[4] Ber. d. chem. Ges., **32**, 1239.

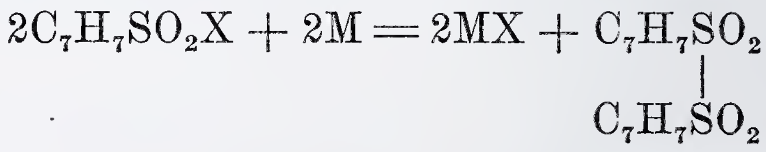
$$\begin{array}{c} RSO_2 \\ | \\ RSO_2 \end{array}$$

A disulphone of this type would be especially interesting because it would differ from all known organic sulphur compounds in having two hexavalent sulphur atoms in direct union. It is known that organic compounds containing two sulphur atoms in direct union, are capable of existence. The aliphatic and aromatic disulphides, for example, are stable substances containing two bivalent sulphur atoms in direct union: R-S-SR. The well crystallized thio ethers, or disulphoxides, $\begin{array}{c} RSO_2, \\ | \\ RS \end{array}$ undoubtedly also contain two sulphur atoms in direct union, and one of the sulphur atoms must be hexavalent, while the other is bivalent. There seems to be no reason, therefore, why compounds containing two hexavalent sulphur atoms should not be capable of existence.

It has been the object of this investigation to determine whether such substances are capable of existing and, if possible, to prepare and study disulphones of the type represented by the formula,

$$\begin{array}{c} RSO_2 \\ | \\ RSO_2 \end{array}$$

Several previous attempts have been made to secure this class of substances. Otto, whose name is so intimately associated with all classes of sulphones, attempted to prepare α, β-disulphones by the methods used for linking carbon atoms together. It was expected that, on the removal of the halogen from two molecules of a sulphone halide, the residues would unite to form a disulphone:[5]



$$2C_7H_7SO_2X + 2M = 2MX + \begin{array}{c} C_7H_7SO_2 \\ | \\ C_7H_7SO_2 \end{array}$$

Otto found, however, that the reactions which take place when sulphone halides are treated with metals, are much more complicated than that represented by this equation, and that they do not lead to the formation of the desired sulphone. Thus, benzenesulphone chloride, when treated with sodium, gave sodium benzenesulphinate:

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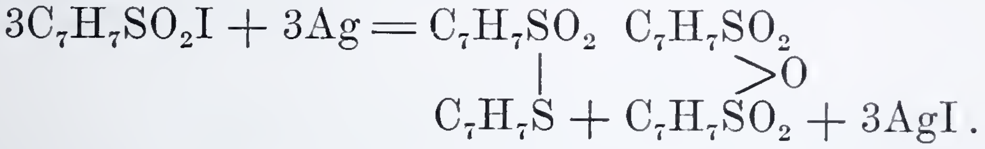
[5] Ber. d. chem. Ges., **24**, 478.

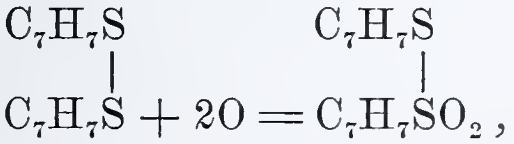
$$C_6H_5SO_2Cl + 2Na = C_6H_5SO_2Na + NaCl,$$

while toluenesulphone iodide, when heated with finely divided silver, reacted according to the equation:



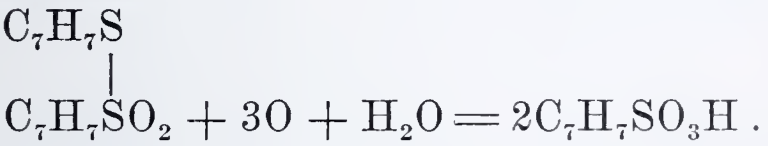
$$3C_7H_7SO_2I + 3Ag = \begin{array}{c} C_7H_7SO_2 \\ | \\ C_7H_7S \end{array} + \left.\begin{array}{l} C_7H_7SO_2 \\ C_7H_7SO_2 \end{array}\right> O + 3AgI\,.$$

It would also seem possible to obtain such sulphones by the oxidation of the disulphides RS.SR, but by this method only one of the sulphur atoms is oxidized to the hexavalent condition, the reaction resulting in the formation of a thio-ether:



$$\begin{array}{c} C_7H_7S \\ | \\ C_7H_7S \end{array} + 2O = \begin{array}{c} C_7H_7S \\ | \\ C_7H_7SO_2 \end{array},$$

On further oxidation the union between the sulphur atoms is broken:

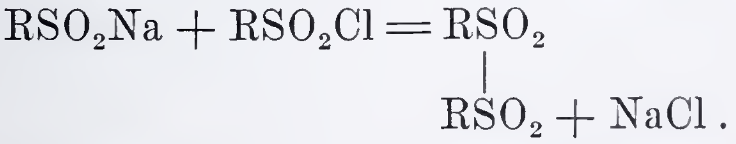


$$\begin{array}{c} C_7H_7S \\ | \\ C_7H_7SO_2 \end{array} + 3O + H_2O = 2C_7H_7SO_3H\,.$$

The failure of these attempts to prepare the disulphone by the methods applicable in the case of carbon compounds led Otto[6] to conclude that these substances are incapable of existence. A more recent investigator[7] has arrived at the same conclusion. All that these results show, however, is that these disulphones can not be made by the methods regularly used for establishing carbon linkages.

Of all possible methods of preparation the following seemed most likely to lead to the desired result.

1. Reaction between a sulphinate and a sulphone halide, thus:



$$RSO_2Na + RSO_2Cl = \begin{array}{c} RSO_2 \\ | \\ RSO_2 \end{array} + NaCl\,.$$

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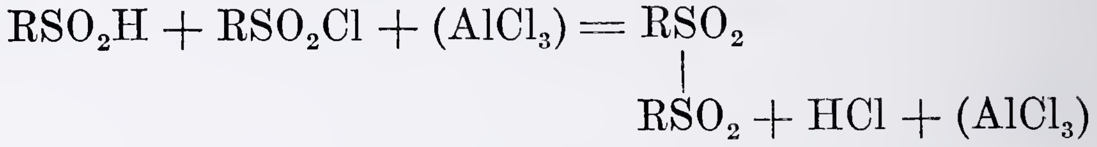
[6] Ber. d. chem. Ges., **24**, 484.

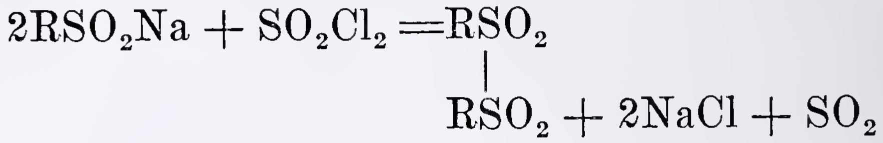
[7] Turner, Amer. Chem. Jour., **21**, 125.

2. Reaction between a sulphinic acid a sulphone halide in the presence of aluminium chloride:



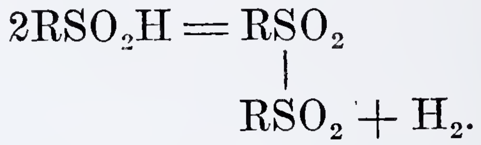
$$\mathrm{RSO_2H + RSO_2Cl + (AlCl_3) = \begin{array}{l} RSO_2 \\ \ | \\ RSO_2 + HCl + (AlCl_3) \end{array}}$$

3. Reaction between a sulphinate and sulphuryl chloride.



$$\mathrm{2RSO_2Na + SO_2Cl_2 = \begin{array}{l} RSO_2 \\ \ | \\ RSO_2 + 2NaCl + SO_2 \end{array}}$$

4. The electrolysis of a sulphinic acid, or its salt.



$$\mathrm{2RSO_2H = \begin{array}{l} RSO_2 \\ \ | \\ RSO_2 + H_2. \end{array}}$$

All of these four methods were tested but failed, with one exception, to give a substance of the desired composition. The reaction between a sulphinate and a sulphone halide, however, gave the class of disulphones expected, and was, therefore, studied in detail.

Reaction Between Sulphinates and Sulphone Chlorides.

1. *Without the use of a solvent.*

A finely ground mixture of equivalent quantities of sodium para-tolylsulphinate and para-tolylsulphone chloride was heated on a waterbath at 70° for several hours without effect. A paraffiin bath was therefore substituted for the water-bath and the temperature raised to 130°-135°. Samples of the pasty mass were removed from time to time and examined for a disulphone. The heating was continued until decomposition began. After washing with water and ammonia a very small quantity of a solid, which was not a disulphone, and an oily substance remained.

2. *In ethereal solution.*

Para-tolylsulphone chloride was dissolved in ether and to this solution an equivalent quantity of powdered sodium para-tolylsulphinate, suspended in ether, was added. There was no action in the cold. The mixture was heated on the water-bath with a return condenser for several days without the formation of any disulphone. A similar mixture was heated in a sealed tube to 100° for eight hours, and to 120°-130° for eight hours more. Decomposition took place, but no disulphone was formed.

3. *In alcoholic solution.*

To a concentrated solution of sodium para-tolylsulphinate in absolute alcohol, an equivalent amount of para-tolylsulphone chloride was added, and the mixture kept at the boiling point of alcohol for several hours. There was no appearance of a disulphone at any time.

4. *In aqueous solution.*

Sodium para-tolylsulphinate was dissolved in the least possible quantity of water. A proportional amount of powdered para-tolylsulphone chloride was added to this solution. The mixture was heated on the water-bath to 70.° At this temperature the chloride melted. The contents of the flask were well shaken, and the chloride almost immediately disappeared. The disappearance of the chloride was followed by the separation of a solid. This solid product was placed on a filter, washed repeatedly with boiling water and finally with ether, dried, and weighed. The yield of crude product was 20 per cent of that calculated according to the equation:

$$C_7H_7SO_2Na + C_7H_7SO_2Cl = C_{14}H_{14}S_2O_4 + NaCl\,.$$

The crude product was not, however, as pure as it was desirable to have it.

5. *In ether and water.*

Para-tolylsulphone chloride was dissolved in a flask in the smallest possible quantity of ether and to this was added a saturated water solution of the calculated amount of sodium para-tolylsulphinate. The flask, which was connected with a return condenser, was heated on a water-bath, and shaken occasionally. In a short time a solid appeared as a scum between the two layers of liquid. The heating was continued until no more solid seemed to form, or until the sulphone chloride had disappeared. The duration of the heating varied in different experiments from six to thirty hours. Although continued heating was apparently necessary, it could not be determined that time entered as a definite factor into the reaction. The hot solution was filtered, and after the evaporation of the ether, was found to contain sulphinic acid. This was neutralized with sodium carbonate, more of the sulphone chloride in ether solution was added, and the mixture again heated. A small additional quantity of the solid product usually separated out.

The filtrate was acidified with sulphuric acid and the sulphinic acid precipitated. This was filtered off, and the filtrate extracted with ether for the removal of any sulphinic acid that had escaped precipitation. This was identified by its melting point. The extracted solution was neutralized with sodium hydroxide and evaporated to dryness. The residue was then extracted with absolute alcohol. The sodium sulphonate thus obtained was acidified and the melting point of the acid determined. The filtrate from the disulphone contained therefore, para-tolylsulphonic acid, para-tolylsulphinic acid and sodium chloride.

The solid, after being washed repeatedly with boiling water to remove any adherent sodium para-tolylsulphinate, dried on the water-bath and washed with boiling ether to extract any unchanged para-tolylsulphone chloride, is white, crystalline, and comparatively pure.

While this method gave an unusually pure product, the yield was small, as the amount of crude substance was only 12-20 per cent of that calculated. With the hope of improving the yield, sulphinates of other metals were prepared and substituted for the sodium sulphinate.

6. *Zinc para-tolylsulphinate and para-tolylsulphone chloride.*

The zinc salt was prepared by reducing the chloride with zinc dust and recrystallizing the product from large quantities of water. A calculated amount of zinc para-tolylsulphinate was added to an ether solution of a weighed quantity of para-tolylsulphone chloride. To this was added a mixture of alcohol and water. The final mixture was heated on the water-bath for an hour, and then allowed to stand over night at the temperature of the laboratory. The zinc sulphinate dissolved, and a very small quantity of disulphone formed. The yield was very poor—the crude product was mixed with much unchanged zinc sulphinate.

7. *Ammonium para-tolylsulphinate and para-tolylsulphone chloride.*

The ammonium salt of para-tolylsulphinic acid was prepared by dissolving the acid in dilute ammonia. It crystallized from this solution in beautiful, colorless, transparent, monoclinic crystals with a melting point of 164°-167°. When recrystallized from water, the melting point remained 164°-167°, bubbles of gas being evolved above 164°.

A concentrated water solution of ammonium para-tolylsulphinate was added to an ether solution of the sulphone chloride. After the mixture was heated for several hours a small quantity of the di-sulphone appeared. This did not increase in amount after the first day, although the heating was continued for six days. After the product was washed with water and ether, it was comparatively pure but small in quantity, the yield being only about 4.5 per cent.

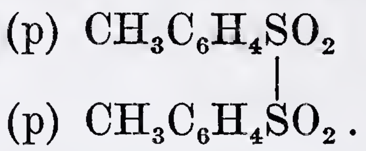
8. *Silver para-tolylsulphinate and para-tolylsulphone chloride.*

The silver sulphinate was prepared by adding a slight excess of silver nitrate to a solution of the sodium salt. It separated as a white, amorphous precipitate, which was filtered and dried with difficulty. Silver para-tolylsulphinate is a white powder, very sensitive to light. It is insoluble in water, methyl alcohol, ethyl alcohol, ether, chloroform and benzene; hence it was not recrystallized. The preparation used in the following experiment was almost white and non-crystalline.

A mixture of equivalent quantities of para-tolylsulphone chloride in ether solution and silver para-tolylsulphinate in a volume of water equal to twice that of the ether, was heated in a flask with a return condenser. The temperature was kept at that of boiling ether for several days. There was apparently no action except the decomposition of the sulphone chloride by the water, and of the silver salt by the light. No reaction between the sulphone chloride and silver salt, resulting in the formation of the di-sulphone, took place. The failure to react may be due to the insolubility of the silver sulphinate.

The amount of di-sulphone resulting from zinc sulphinate, ammonium sulphinate, or silver sulphinate was, in every instance, less than that obtained from sodium sulphinate. The sodium sulphinate was, therefore, considered the best salt to use in the preparation of the di-sulphones.

I. Di-paratolyldisulphone.



$$\begin{array}{l}\text{(p) } CH_3C_6H_4SO_2 \\ \qquad\qquad\qquad\quad | \\ \text{(p) } CH_3C_6H_4SO_2\,.\end{array}$$

As a result of the experiments already described, and of others, the method adopted for the preparation of di-paratolyldisulphone was as follows:

Fifty-five grams sodium para-tolylsulphinate was dissolved in the least possible quantity of water. This was added to 58.3 grams para-tolylsulphone chloride dissolved in the least possible quantity of ether. The flask containing the mixture was fitted with a return condenser and heated on the water-bath. The temperature was kept at the boiling point of ether until there was no longer any unchanged sulphone chloride. The hot solution was filtered, after the evaporation of the ether. The white, crystalline solid was washed repeatedly with boiling water, dried on the water-bath, and washed with ether, with which it was allowed to stand in contact for about twenty-four hours with occasional agitation. It was then put upon a filter, washed with ether and dried. The crude di-sulphone was dissolved in boiling benzene, from which most of it crystallized on cooling. The remainder was obtained by the evaporation of the benzene, and was recrystallized from benzene. Since the substance still contained a small quantity of the sulphone chloride, the two portions were again washed with ether, redissolved in boiling benzene and allowed to crystallize as before. The weight of this purified product was 15 grams. The theoretical yield from 55 grams sodium para-tolylsulphinate is 84 grams. The yield of purified di-sulphone was, therefore, 18 per cent.

Di-paratolyldisulphone is a white, crystalline solid insoluble in water, methyl alcohol or ethyl alcohol. It is very difficultly soluble in chloroform, more soluble in boiling benzene or glacial acetic acid. Of the last two solvents, benzene is probably the better. The substance separates on cooling its benzene solution, in small lustrous plates that adhere to the sides and bottom of the vessel. By the spontaneous evaporation of the cold solution, or the slow cooling of the boiling solution, the crystals may attain a diameter of 5-6 millimeters. They are thick monoclinic tables, very brittle and harder than sodium chloride. The substance melts with decomposition at 220°.

An analysis of the substance gave the following results:

I. 0.1551 gram substance gave 0.3073 gram CO_2 and 0.0597 gram H_2O.

II. 0.1609 gram substance gave 0.3196 gram CO_2 and 0.0621 gram H_2O.

III. 0.1273 gram substance gave 0.2041 gram $BaSO_4$.

IV. 0.1960 gram substance gave 0.2919 gram $BaSO_4$.

V. 0.1503 gram substance gave 0.2259 gram $BaSO_4$.

	Calculated for $(C_7H_7SO_2)_2$	Found. I.	 II.	 III.	 IV.	 V.
C	54.19	53.9	54.1			
H	4.51	4.26	4.3			
S	20.64			20.49	20.45	20.64

A molecular weight determination by the cryoscopic method with naphthalene as the solvent, gave the following results:

I. 1.63 grams substance per 100 grams of solvent gave a mean depression of 0.355°.

II. 2.53 grams substance per 100 grams of solvent gave a mean depression of 0.565°.

III. Constant for naphthalene, 70.

	Calculated for $(C_7H_7SO_2)_2$	Found. I.	 II.
Molecular weight	310.0	321.0	313.0

Di-paratolyldisulphone is remarkable for its inertness. It is not decomposed by mineral acids under ordinary conditions of temperature and pressure. At ordinary pressure the substance is not affected in the least degree by concentrated hydrochloric acid. Two-tenths of one gram of the powdered di-sulphone of melting point 220°, was boiled with 20 cubic centimeters concentrated hydrochloric acid for five hours without decomposition. After dilution with water the liquid was filtered off and the solid washed with water, dried and weighed. The result was 0.195 gram of solid which melted at 220°.

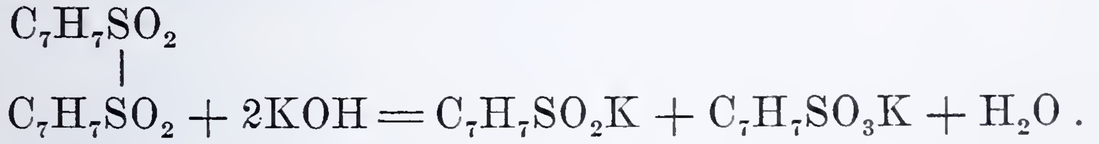
Decomposition is, however, effected by heating the di-sulphone with concentrated hydrochloric acid under pressure. After 0.8 gram of substance and 20 cubic centimeters of concentrated hydrochloric acid were put in a tube, the tube was sealed and heated in a bomb-furnace for about six hours to 110°-120°, and for eight hours to 120°-130° without any change in the appearance of the contents of the tube. After the mixture had stood for forty hours there were a few small brown patches, which gave evidence of some reaction. The heating to 125°-130° was continued for seven hours longer, and the tube allowed to stand for two days. When opened it showed diminished pressure. Addition of water to the acid and brown oily mass caused the separation of a white solid, which, when freed from the oily substance, washed, and recrystallized from benzene, gave a melting point of 218°, with decomposition. It was unchanged di-sulphone. The oily mass consisted of a brown tar, para-tolylsulphinic acid melting at 84°, para-tolylsulphonic acid melting at 92°, and a little inorganic material. The tar, which possessed a cresol-like odor, was distilled with steam, but the quantity was too small to permit of any decisive test.

Di-paratolyldisulphone is difficultly soluble in boiling concentrated nitric acid, and crystallizes from this solution unchanged. Two-tenths of one gram of the di-sulphone was dissolved in 75-100 cubic centimeters of concentrated nitric acid. One hundred and sixty-four thousandths of a gram of substance melting with decomposition at 220° crystallized from this nitric acid solution on standing for a short time. The mother liquor, on evaporation, deposited a less pure substance, weighing 0.03 gram, and melting with decomposition at 217°. Protracted contact with fuming nitric acid led to the oxidation of the di-sulphone to carbon dioxide, water, and sulphuric acid.

When treated with fuming sulphuric acid in the cold, the di-sulphone immediately dissolved, giving a red-brown solution. This solution became milky when poured into water. From the diluted solution, sulphinic acid was extracted with ether and identified by its melting point. The acid solution, after extraction, was neutralized with sodium hydroxide, evaporated to dryness and extracted with absolute alcohol, but no sodium para-tolylsulphonate was found. While the reaction is not a simple one, sulphinic acid constitutes the principal product. The decomposition with fuming sulphuric acid is therefore, similar to that effected by concentrated hydrochloric acid in a sealed tube.

A mixture of concentrated sulphuric and nitric acids brought about no decomposition, even when heated. The substance was merely less soluble in the mixture than in concentrated nitric acid alone.

Di-paratolyldisulphone is not attacked by alkalies in the cold, but is decomposed by boiling concentrated potash. One and one-half grams of the di-sulphone was boiled with 4 cubic centimeters of potassium hydroxide (2:3) for twenty minutes. Small quantities of water were added to supply that lost by evaporation. The di-sulphone dissolved completely. A portion of the solution was treated with zinc and acid. A strong odor of mercaptan resulted, indicating the presence of a sulphinic acid. The ether extract of the acidified solution deposited para-tolylsulphinic acid, which melted at 85°-86°. The acid solution was neutralized and evaporated to dryness. The residue was extracted with absolute alcohol. A water solution of the sodium para-tolylsulphonate which crystallized from the alcohol solution, was acidified with sulphuric acid. From this solution para-tolylsulphonic acid, melting at 91°, separated. This was dried and treated with phosphorus pentachloride. The resulting sulphone chloride, after crystallization from ether, melted at 68°-69°, the melting point of para-tolylsulphone chloride. The decomposition with alkalies must therefore be in accordance with the equation:



$$\begin{array}{l} C_7H_7SO_2 \\ \quad | \\ C_7H_7SO_2 + 2KOH = C_7H_7SO_2K + C_7H_7SO_3K + H_2O\,. \end{array}$$

All attempts to effect a decomposition by boiling with water, or with very dilute alkalies, failed, although the boiling was continued for seven or eight hours.

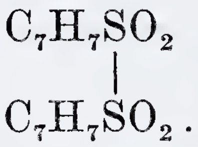
An attempt was made to oxidize di-paratolyldisulphone, in acetic acid solution, with potassium permanganate solution, but without success. Into a hot solution of 2 grams di-sulphone in acetic acid, 300 cubic centimeters of a 5 per cent solution of potassium permanganate was slowly dropped as fast as the solution became colorless. After about forty hours the process was stopped and the clear solution filtered off. Nothing but a small quantity of inorganic matter was found in the acid solution. The oxides of manganese were extracted with boiling benzene, and 1.9 grams of the unchanged di-sulphone crystallized out. After recrystallization from benzene the di-sulphone melted with decomposition at 220°. A blank test was made with some of the same acetic acid and potassium permanganate solution. Decoloration took place about as rapidly as when the di-sulphone was present. The reduction of the permanganate was therefore due to the acetic acid and not to the di-sulphone.

Proof of Structure.

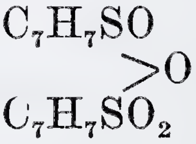
The formation of the solid substance, described as di-sulphone, undoubtedly takes place according to the equation:

$$C_7H_7SO_2Na + C_7H_7SO_2Cl = C_{14}H_{14}S_2O_4 + NaCl\,.$$

That this reaction does not take place in the absence of water, and that a very small quantity of water is sufficient has been demonstrated, but it has not been possible to determine what rôle the water plays. The reaction, however, supplies a clue to the structure of the product. Two possibilities present themselves, depending on the desmotropic nature of sulphinic acids. If the sulphinate reacts according to the generally accepted formula, $C_7H_7S\underset{\diagdown Na}{O_2}$, then the product must be a di-sulphone with the structure represented by the formula:


I.
$$\begin{array}{c} C_7H_7SO_2 \\ | \\ C_7H_7SO_2\,. \end{array}$$

If, however, the formula of the sulphinate is $C_7H_7S\underset{\diagdown ONa}{O}$,[8] then the substance might be an anhydride with the structure represented by the formula:


II.
$$\begin{array}{l} C_7H_7SO \\ \qquad\quad >O \\ C_7H_7SO_2 \end{array}$$

The anhydrides of sulphonic acids are, for the most part, extremely reactive substances, similar in behavior to sulphur trioxide, the anhydride of sulphuric acid. They readily react with water and alcohol to form sulphonic acids and sulphonic acid esters. A mixed anhydride of a sulphinic and a sulphonic acid, like that represented by formula II, would be expected to be equally sensitive to these reagents. It has been shown, however, that the substance under consideration is exceedingly inert. It is not hydrolyzed by boiling with water, dilute alkalies or acids. It may even be crystallized unchanged from a solution in concentrated nitric acid. This behavior is in favor of the di-sulphone formula. It would seem incredible that an anhydride containing a sulphinic acid residue could resist hydrolysis and oxidation by concentrated nitric acid.

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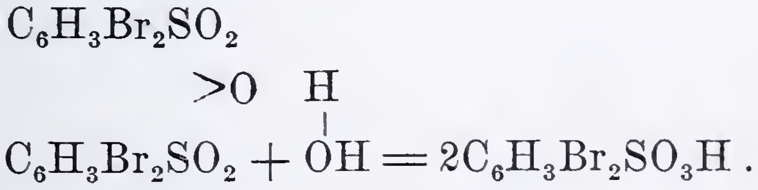
[8] Ber. d. chem. Ges. **18**, 2493.

A peculiar class of anhydrides of sulphonic acids has been described by Rosenberg.[9] Rosenberg found that when para-dibrombenzene is treated with fuming sulphuric acid it is converted into the anhydride of para-brombenzene sulphonic acid, an inert substance melting at a high temperature, insoluble in water, but soluble in alcohol without decomposition. Armstrong [10] found that only sulphonic acids derived from halogen substitution products of benzene form anhydrides of this kind.

For purposes of comparison, para-dibrombenzene sulphonic anhydride was made by the method of Rosenberg, modified as follows: A mixture of di-brombenzene and fuming sulphuric acid in the proportion of 2 grams of the former to 6.5 cubic centimeters of the latter was heated in a flask supplied with an internal condenser, until there was no further separation of solid from the reddish-brown solution. The product was poured into ice-water, and washed with cold water until the wash-water no longer had an acid reaction. The white, finely crystalline anhydride was purified by recrystallization from alcohol and benzene. After purification, the anhydride was boiled with water, alkalies, and acids. It was found that, while the substance is remarkably stable towards water, it is hydrolyzed by alkalies according to the equation:



$$\left.\begin{array}{l}C_6H_3Br_2SO_2\\C_6H_3Br_2SO_2\end{array}\right>O + \overset{\overset{H}{|}}{O}H = 2C_6H_3Br_2SO_3H\,.$$

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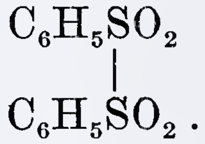
[9] Ber. d. chem. Ges. **19**, 652.

[10] Proc. Chem. Soc., 1892, 42.

There is a marked difference between the behavior of the anhydride and the substance under investigation towards acids. The former, as was to be expected, is readily hydrolyzed by acids, while the latter can be boiled with concentrated hydrochloric acid or crystallized from concentrated nitric acid without undergoing change. In view of these facts the di-sulphone formula must be accepted as the more probable, although it was not possible definitely to disprove the anhydride formula.

II. Diphenyldisulphone.



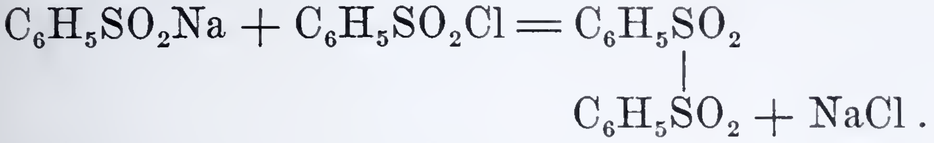
$$\begin{array}{c} C_6H_5SO_2 \\ | \\ C_6H_5SO_2\,. \end{array}$$

From benzene sulphone chloride and sodium benzene sulphinate.

The sulphinate was prepared by the reduction of the sulphone chloride with zinc dust, and purified by crystallization from water. Benzene sulphone chloride was added to an equivalent quantity of sodium benzene sulphinate in water solution. The mixture was heated to the temperature of a boiling water-bath until there seemed to be no more action. As in the preparation of diparatolyldisulphone, the substance formed more or less slowly as a white, crystalline, insoluble scum. When the scum no longer increased in amount, the hot solution was filtered. The filtrate contained, besides sodium chloride, some unchanged sulphone chloride, sodium benzene sulphinate, benzene sulphinic acid, and benzene sulphonic acid. The solid was washed with boiling water and ether, and purified by recrystallization from benzene.

All attempts to prepare the diphenyldisulphone in the absence of water, failed. In some preparations the sulphone chloride was dissolved in ether. The yield was not improved by this modification; the reaction, however, proceeded somewhat more rapidly. In no case was the yield more than 20 per cent, nor less than 10 per cent, of the theoretical amount. Other modifications were introduced in the method of preparation with a view to increasing the yield, but without success. No di-sulphone was formed in those experiments in which an excess of sulphone chloride, or of sodium sulphinate was used.

The equation representing the formation of diphenyldisulphone is in all probability:



$$C_6H_5SO_2Na + C_6H_5SO_2Cl = \begin{array}{l} C_6H_5SO_2 \\ \quad | \\ C_6H_5SO_2 + NaCl\,. \end{array}$$

The formation is, therefore, exactly analogous to that of diparatolyldisulphone. It has also been determined in this case that water is indispensable to the reaction. Thus, a mixture of benzene sulphone chloride and sodium benzene sulphinate in equivalent quantities was heated for several hours without the formation of di-sulphone. Almost immediately on the addition of a few drops of water the di-sulphone began to form.

Like diparatolyldisulphone, diphenyldisulphone is a white, beautifully crystalline substance, insoluble in water and but slightly soluble in ether. It is moderately soluble in chloroform and readily soluble in benzene, from which it crystallizes in small, well defined tables. In order to obtain an absolutely pure substance it is necessary to wash the finely powdered substance many times in hot ether, and recrystallize several times from benzene. The melting point of the pure diphenyldisulphone is 185°-186°. It melts, unlike diparatolyldisulphone, without decomposition; the melted substance remaining clear with only a very slight brown tint, until the temperature reaches 200°, when the whole becomes black.

An analysis of the substance gave the following results:

I. 0.2198 gram substance gave 0.4050 gram CO_2.

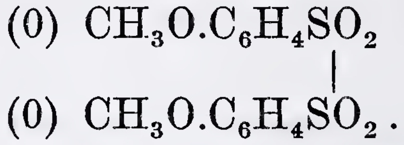
II. 0.2158 gram substance gave 0.3982 gram CO_2, and 0.0672 gram H_2O.

III. 0.2573 gram substance gave 0.4799 gram CO_2, and 0.0814 gram H_2O.

	Calculated for $(C_6H_5SO_2)_2$	Found. I.	II.	III.
C	51.06	50.50	50.37	50.83
H	3.54		3.47	3.51

Diphenyldisulphone is more easily decomposed by reagents than diparatolyldisulphone. If boiled with water for several hours it dissolves completely with entire decomposition. Five-tenths of one gram of the substance was boiled for three hours with 15-20 cubic centimeters of water, accomplishing complete decomposition. This solution contained benzene sulphinic acid, identified by its reaction with zinc and acid, and benzene sulphonic acid, identified by its melting point, which was 43°.

III. Diorthoanisoldisulphone.



$$\begin{array}{l}(0)\ \mathrm{CH_3O.C_6H_4SO_2}\\ \qquad\qquad\qquad\qquad\ \ |\\ (0)\ \mathrm{CH_3O.C_6H_4SO_2}\,.\end{array}$$

This substance was made from ortho-anisolsulphone chloride and sodium ortho-anisolsulphinate.

The sulphinate was made from ortho-anisidine according to the method of Gattermann[11] for preparing sulphinic acids. The sulphone chloride was prepared from the sulphinic acid. It had been observed that a sulphone chloride is one of the reaction products when sulphuryl chloride reacts with a sulphinate in the presence of water.

$$C_7H_7SO_2Na + SO_2Cl_2 = C_7H_7SO_2Cl + NaCl + SO_2\,.$$

This suggested a method for the preparation of sulphone chlorides, and, in so far as it has been tested, it has proved a very general reaction.

The details of the process are as follows: Sulphuryl chloride was slowly added from a dropping funnel to an ether solution of an equivalent quantity of a sulphinic acid with a constant agitation of the liquid. If enough heat was given off to make the flask feel warm to the hand, it was cooled by holding it in a stream of cold water. This was, however, not always necessary. The addition of a small quantity of water before or after the adding the sulphuryl chloride, was found to be advantageous, but the presence of water is not essential to the reaction. The sulphone chloride crystallized from the ether solution, on evaporation, in a comparatively pure condition. The quality of the product was much improved by shaking the ether solution with an equal volume of water, and separating the two solutions after half an hour's standing. The water solution was acid and possessed a strong odor of sulphur dioxide. The reaction involved in the formation of the sulphone chloride may be represented by the equation:

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[11] Ber. d. chem. Ges., **32**, 1141.

$$CH_3O.C_6H_4SO_2H + SO_2Cl_2 = CH_3O.C_6H_4SO_2Cl + HCl + SO_2 .$$

The yield of sulphone chloride was in every instance good. Ten grams ortho-anisolsulphinic acid gave 10.5 grams sulphone chloride after one recrystallization from ether. In this preparation the crude product melted at 55°-57°, after one recrystallization from ether it melted at 55°. The correct melting point of ortho-anisolsulphone chloride is 55°.

The applicability of this method was tested in the preparation of para-tolylsulphone chloride, ortho-anisolsulphone chloride, *a*, naphthalenesulphone chloride, and meta-xylenesulphone chloride, with equally good results in all cases. Since Gattermann's method for preparing sulphinic acids may be so generally and successfully employed, the above method for making sulphone chlorides of definite structure will be found most convenient.

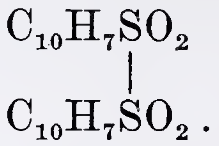
Diorthoanisoldisulphone was prepared by the continued heating of a mixture of equivalent quantities of ortho-anisolsulphone chloride in ether solution, and sodium ortho-anisolsulphinate in water solution. The substance is, in appearance, much like the two di-sulphones already described. It separates as it is formed in much the same way. It crystallizes well from benzene, which is the best solvent for it. Its one impurity, sulphone chloride, was removed with some difficulty, by repeated washings with ether and recrystallization from benzene. The melting point obtained for diorthoanisoldisulphone was 184°-185° with decomposition. The yield was small, averaging about 10 per cent. All attempts to increase the yield by modifying the conditions were unsuccessful.

An analysis of the substance gave the following results:

I. 0.1010 gram substance gave 0.1806 gram CO_2, and 0.0360 gram H_2O.

	Calculated for $(CH_3OC_6H_4SO_2)_2$	Found. I.
C	49.12	48.71
H	4.09	3.96

IV. DI-NAPHTHALENEDISULPHONE.

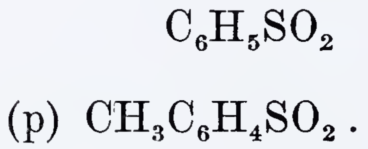


$$\begin{array}{c} C_{10}H_7SO_2 \\ | \\ C_{10}H_7SO_2\,. \end{array}$$

The sulphone was made from α-naphthalene sulphone chloride and sodium α-naphthalene sulphinate.

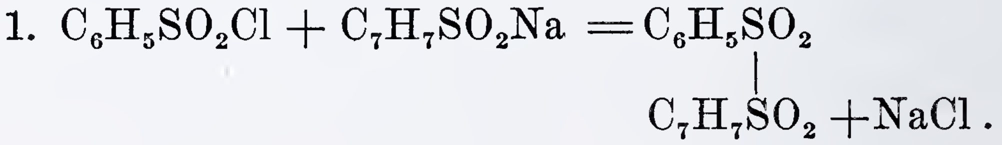
The sulphinic acid was prepared according to the Gattermann method, and the sulphone chloride from the acid by treatment with sulphuryl chloride according to the method already described under diorthoanisoldisulphone. A mixture of equivalent quantities of ortho-anisolsulphone chloride in ether solution, and sodium ortho-anisolsulphinate in water solution, was heated until there was no longer any reaction. The substance separated out as described in the preparation of other di-sulphones. It closely resembles them in appearance, being, however, slightly colored, but less so than ortho-anisolsulphinic acid, which has a decidedly yellow tint. Although soluble in benzene, it does not crystallize well from this solvent. The substance also readily dissolves in nitrobenzene, and is partially deposited from its solution in this solvent as a crystalline powder. The melting point of the crystals from benzene solution was found to be 184°-186°, with decomposition.

V. PHENYL-PARATOLYLDISULPHONE.

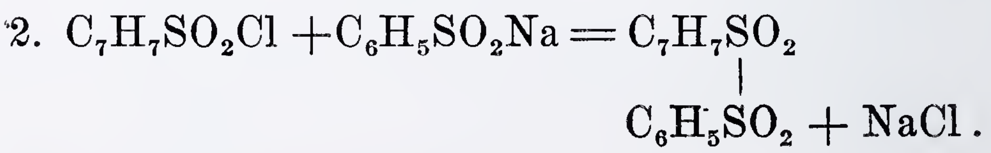


$$\begin{array}{l} \quad C_6H_5SO_2 \\ \\ (p)\ CH_3C_6H_4SO_2\,. \end{array}$$

This was prepared from benzenesulphone chloride and sodium para-tolylsulphinate, and also from para-tolylsulphone chloride and sodium benzenesulphinate.

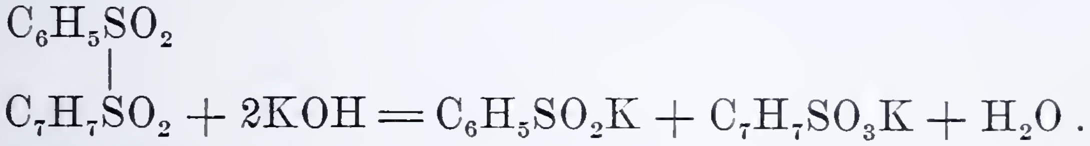


$$1.\ C_6H_5SO_2Cl + C_7H_7SO_2Na = \begin{array}{l} C_6H_5SO_2 \\ \quad | \\ C_7H_7SO_2 + NaCl\,. \end{array}$$

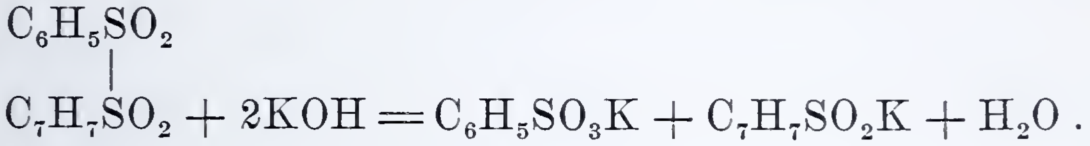


$$2.\ C_7H_7SO_2Cl + C_6H_5SO_2Na = \begin{array}{l} C_7H_7SO_2 \\ \quad | \\ C_6H_5SO_2 + NaCl\,. \end{array}$$

The substance is a white solid very similar to diparatolyldisulphone in crystalline form, but dissolves more easily in ether and benzene, and is readily soluble in chloroform. Its melting point is 166°. Phenylparatolyldisulphone is decomposed by boiling caustic potash. Potassium chloride, potassium benzenesulphonate, potassium benzenesulphinate, potassium tolylsulphinate, and potassium tolylsulphonate were found in the diluted solution. Its decomposition may be represented by the equations:

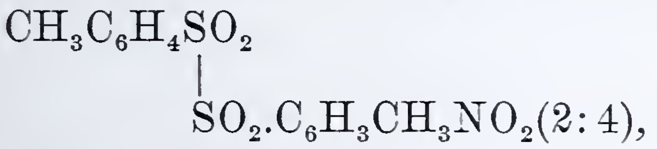
1. 

$$\begin{array}{l} C_6H_5SO_2 \\ \quad | \\ C_7H_7SO_2 + 2KOH = C_6H_5SO_2K + C_7H_7SO_3K + H_2O\,. \end{array}$$

2. 

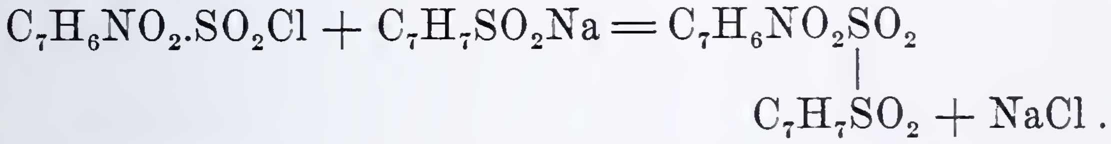
$$\begin{array}{l} C_6H_5SO_2 \\ \quad | \\ C_7H_7SO_2 + 2KOH = C_6H_5SO_3K + C_7H_7SO_2K + H_2O\,. \end{array}$$

VI. PARATOLYLPARANITROORTHOTOLYLDISULPHONE.

(4) 

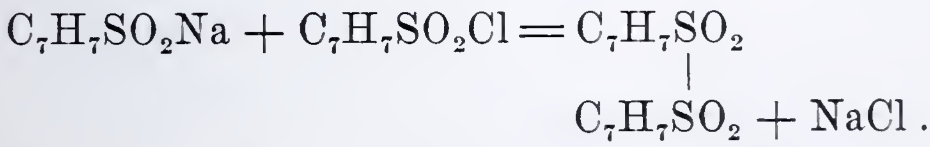
$$\begin{array}{l} CH_3C_6H_4SO_2 \\ \qquad\quad | \\ \qquad\quad SO_2.C_6H_3CH_3NO_2(2:4), \end{array}$$

was prepared from sodium para-tolylsulphinate and paranitro-orthotolylsulphone chloride. In the preparation of this substance, by heating an ether solution of the sulphone chloride and a water solution of the sodium sulphinate, mixed in equivalent amounts, diparatolyldisulphone was also formed. This would indicate a secondary reaction between the sulphone chloride and the sulphinate similar to the reaction between sulphuryl chloride and sulphinic acid.

1. 

$$\begin{array}{l} C_7H_6NO_2.SO_2Cl + C_7H_7SO_2Na = C_7H_6NO_2SO_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad C_7H_7SO_2 + NaCl\,. \end{array}$$

2. $C_7H_6NO_2SO_2Cl + C_7H_7SO_2Na = C_7H_6NO_2SO_2Na$
$+ C_7H_7SO_2Cl\,.$

3. 

$$\begin{array}{l} C_7H_7SO_2Na + C_7H_7SO_2Cl = C_7H_7SO_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad C_7H_7SO_2 + NaCl\,. \end{array}$$

The two substances being almost equally soluble, crystallized together from benzene, the paratolylparanitroorthotolyldisulphone in thick, slightly colored prisms. This difference in the appearance of the two substances made it possible to separate the two kinds of crystals, and by fractional crystallization from chloroform the paratolylparanitroorthotolyldisulphone was obtained in a pure condition. It melts at 154°.

No combustions of the last three substances were made because of the limited amount of material. There is, however, sufficient reason for believing they were obtained in a pure condition, and that the melting points are correct.

Conclusion.

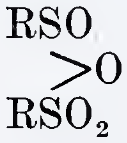
The experiments described above show that 1, 2 di-sulphones, while difficult to make, are capable of existence, and, therefore, that it is possible to get organic sulphur compounds that contain two hexavalent sulphur atoms in direct union. The evidence on which this statement is based is as follows:

By the reaction between sulphone chlorides and sulphinates substances are formed whose composition and molecular weight are represented by the general formula $(RSO_2)_2$. The reaction by which these substances are formed must, therefore, be represented by the equation:

$$RSO_2Cl + RSO_2Na = (RSO_2)_2 + NaCl.$$

There are but two possible structural formulas for a substance formed according to this equation,

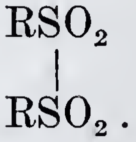
I.



$$\begin{matrix}RSO\\ \quad >O\\ RSO_2\end{matrix}$$

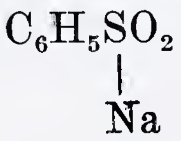
and

II.



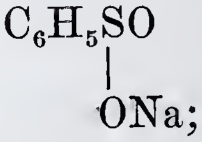
$$\begin{matrix}RSO_2\\ |\\ RSO_2\end{matrix}.$$

The method of preparation does not supply any basis on which to decide between these formulas because it is not known whether the sulphinate reacts as



$$\begin{matrix}C_6H_5SO_2\\ |\\ Na\end{matrix}$$

or as



$$\begin{matrix}C_6H_5SO\\ |\\ ONa\end{matrix};$$

and the matter is complicated by the fact that the reaction takes place only in the presence of water.

Formula I represents a mixed anhydride of a sulphonic and a sulphinic acid. Anhydrides of sulphonic acids and mixed anhydrides of sulphonic acids and carbonic acids are known. These are all readily hydrolyzed by acids and alkalies. Quite the opposite of this is the case with the substances under consideration. Acids apparently do not hydrolyze them at all. When heated with concentrated hydrochloric acid in sealed tubes they are ultimately decomposed, but the process is not hydrolysis. When boiled with alkalies, they are decomposed into sulphinates and sulphonates. The process is one of hydrolysis:

$$(RSO_2)_2 = RSO_2H + RSO_3H ,$$

but takes place with much greater difficulty than would be expected in any anhydride containing a sulphonic acid residue.

Formula I also represents a substance containg a sulphinic acid residue. All known sulphinic acids are easily oxidized. It would be expected, therefore, that a substance with this formula would behave in the same way. The substances under consideration, however, are extremely stable in the presence of oxidizing agents. Potassium permanganate has no action on them, and they can be crystallized from concentrated nitric acid without loss. Formula I does not agree with the properties of the substances.

Formula II represents a di-sulphone. Sulphones, as a class, are marked by great crystallizing power, insolubility in water, high melting and boiling points, stability and inertness. The substances under consideration crystallize in hard, lustrous, perfectly-formed crystals; they are insoluble in water, difficultly soluble in organic solvents; they all melt at a high temperature—most of them with decomposition; they are stable, and, as has been shown, unusually inert. The properties of these substances, therefore, agree with the requirements of formula II; the substances are 1, 2 di-sulphones.

As a result of this investigation a new class of di-sulphones, containing hexavalent sulphur, has been discovered. Several members of the class have been isolated; their properties, both physical and chemical, have been noted; the reactions involved in their formation have been studied; and their constitution has been determined. While too inert to take part in chemical transformations, the 1, 2 di-sulphones are of theoretical importance, since they constitute the missing class in the series of di-sulphones.

LIFE.

In 1893, at the age of twenty-one, I entered the Pennsylvania State College as a special student in chemistry. From 1895 to 1897, I was student assistant in the Chemical Laboratory of Mount Holyoke College. I received the degree of B. S. from that institution in 1898. During the years 1897-99 and 1900-1901, I studied at Bryn Mawr College, holding the Fellowship in Chemistry for the year 1898-99. In 1899-1900 I was granted the Francis Sargent Pepper Fellowship at the University of Pennsylvania.

In my graduate study my major subject was chemistry, while my minor subjects were physiology and physical chemistry. The work in organic chemistry was done with Professor Keiser and Professor Kohler of Bryn Mawr College; that in inorganic chemistry with Professor Smith and others of the University of Pennsylvania. In 1899, I published, with Professor Kohler, an article on "Disulphones and Ketosulphones," and another on "The Reactions Between Sulphone Chlorides and Metallic Derivatives of Ketonic Esters."

The work in physiology was done under Doctor Warren of Bryn Mawr College, and the work in physical chemistry under Professor Smith of the University of Pennsylvania.

At the conclusion of this work, I wish to express my grateful appreciation of the assistance of Professor Kohler, under whom the investigation was carried on.